Dispersed Catalysts for Coal Dissolution

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Introduction

In 1988, one of the authors conducted a review of the status of catalysis in direct coal liquefaction.[1] The objectives were to assess the current state of knowledge and to identify new directions for research. The application of catalysts was addressed with respect to the two-stage processing concept, distinguishing the processes of primary coal dissolution and coal liquids upgrading.

Supported catalysts are quite adequate to the task of hydroprocessing distillate coal liquids. However, in the presence of high-boiling and non-distillable liquids, they are rapidly deactivated by the deposition of carbonaceous materials and metals. Furthermore, since large molecules cannot access the active catalyst surface, supported catalysts can only indirectly influence the processes of coal dissolution and residual coal liquids upgrading.

To surmount these problems, there are several possible approaches to developing new supported catalysts that are less prone to deactivation. However, it is also considered that there is considerable potential for improving liquefaction processing and economics through the development and appropriate application of highly dispersed catalysts. The principle objectives are to promote the process of primary coal dissolution and produce a solubilized product that can be upgraded with greater facility in a second stage over supported catalysts. Dispersed catalysts may also help to realize the potential of using cheap, low-rank coals as feedstocks by increasing the low rates and extent of conversion that are normally attained. Additionally, they may help to lower constraints on solvent quality, facilitating greater flexibility in the selection of recycle solvent fractions and the coprocessing of coals with petroleum residua.

This paper will address the use and development of coal dissolution catalysts. Emphasis will be given to iron-based catalysts because of cost considerations, and to their applicability to the liquefaction of low-rank coals.

Liquefaction of Low-Rank Coals

Before entering a discussion of dispersed catalysts, *per se,* some comments will be addressed to the liquefaction of low-rank coals. The present interest in these coals as liquefaction feedstocks relates to their lower cost, and to their ability to produce higher yields of low molecular weight products than bituminous coals.[2-4] It has been shown by comparative studies of processing bituminous and subbituminous coals that, in the latter case, the rate of deactivation of the second stage supported catalyst is lower and the resid is more reactive.[5] Against this, low-rank coals tend to convert more slowly and to lower ultimate conversions. Pilot plant experience has also shown that these coals can cause severe operating problems through the formation of deposits.[6]

The thermal liquefaction of low-rank coals proceeds with difficulty, due to their normally low content of catalytically active mineral matter and to the high reactivity of the organic structure. The latter allows crosslinking reactions to proceed at moderate temperatures, rendering the coal more difficult to dissolve. However, in the presence of a suitable catalyst, these phenomena can be suppressed and the potential for producing high distillate yields can be realized (Figure 1). [2]

Research by Keogh and Davis [7] has shown that the liquefaction pathways for bituminous coals and subbituminous coals are quite different. The triangular plot in Figure 2 shows the conversion routes followed by these coals from insoluble organic matter, to preasphaltenes and asphaltenes, to oil and gas. These data were developed from microautoclave experiments using a large number of coal samples, donor and nondonor solvents, and various supported and unsupported catalysts. What is found is that the two ranks of coal fall into different bands, and, as discussed above, oils are produced more directly from subbituminous coals, indicative of their being composed of smaller structural units. A second relevant finding is that, for a given coal, none of the variables affects the conversion pathway or conversion selectivity, and the only measurable effect is to increase the conversion kinetics. Thus it seems that selectivity can only be influenced by choice of feedstock, but that appropriate catalysts can improve the rate of conversion.

Dissolution Catalysts

The activity of dissolution catalysts is considered to depend on their composition and the extent of their dispersion and intimate contact with the coal-solvent slurry. These are interrelated factors, since the composition of the catalyst precursor will determine the methods that can be used for its addition and dispersion, and the efficacy of its conversion to an active form.

The extent of dispersion over, and in, the solid coal, and in the coal-solvent slurry, is directly related to the catalyst effectiveness. Until the coal is dissolved, there is no available mechanism by which reactants can be transported to the catalyst, and hence the basic requirement is to transport the catalyst to the reacting species. Overwhelming evidence has accumulated to demonstrate that catalyst activity is enhanced by introducing the precursor in a form more conducive to attaining high dispersion. [8]

There are no really satisfactory techniques for measuring high levels of dispersion. Its attainment and maintenance is inferred from the results of liquefaction experiments, and it is not usually possible to distinguish unequivocally the influence of other factors. For example, the rate of conversion of the precursor to a sufficiently active form may be too slow to influence the process of coal dissolution. The active form of catalysts such as Fe and Mo is generally believed to be a sulfide. In many cases, the attainment of this phase relies upon in-situ sulfiding, and there is scant information on the relative kinetics of dissolution and sulfiding reactions.

While direct comparisons are difficult, it is apparent that, all other things being equal, molybdenum is a much more active catalyst than iron. However, in the absence of suitable methods for catalyst recovery and/or recycle, the cost of Mo is considered prohibitive.

In the developments in Germany in the 1920s and 1930s, finely ground Mo catalysts were first used for the liquid phase hydrogenation of brown coal tar, initially at concentrations as high as 25%.[9] Effective results were subsequently obtained with much lower concentrations of Mo impregnated as ammonium molybdate solution onto brown coal char. Without the ability to separate and recover catalyst, attention was ultimately directed to using lower catalyst concentrations or lower cost catalysts. The impregnation of brown coal with ammonium molybdate allowed a concentration of 0.02% wt. of coal to be used. To reduce cost, iron ores were introduced at higher concentrations (2% wt of coal and higher). Iron compounds supplanted Mo on the brown coal char supports, and the effectiveness of the iron ores was later improved through their partial replacement by impregnating ferrous sulfate directly on the coal, which presumably aided dispersion.

For the same reasons, iron-based catalysts are preferred now, and there are considerable efforts to find means to enhance their activity. Much of this work is of a fundamental

nature and therefore it is not entirely reasonable to require economic justification. Nevertheless, it must be taken into account that the more exotic the preparation, the higher will be the cost, and that this could negate the basis for using iron as a starting point.

Directionally, the main approach to increasing catalytic activity is towards increasing the dispersion of the catalyst precursor and to maintaining this high dispersion after transformation to the active phase. Several techniques have been used to this end including the use of oil soluble organometallics, the synthesis of ultrafine particles, and the application of impregnation techniques to add the iron directly into the coal matrix.

High activities are reportedly favored by catalysts introduced as oil-soluble organometallic precursors such as naphthenates and carbonyls [10-15]. The work of Yamada et al. [13] showed that the catalytic effect of the cyclopentadienyliron dicarbonyl dimer $\{[FeCp(CO)_2]_2\}$ is of the same order of magnitude as that of iron pentacarbonyl. The dicarbonyl dimer at a catalyst loading of 1 wt% Fe of resulted in an increase in conversion to THF solubles from 57% to 93% for an Illinois #6 bituminous coal at 425° C and 711 psig H_2 (cold) for 60 min. This compares favorably to the 92% conversion obtained for the same catalyst loading with the precursor molybdenum hexacarbonyl $\{Mo(CO)_6\}$. The iron pentacarbonyl also showed the same high catalytic activity for a subbituminous Wandoan coal in the presence of added sulfur, resulting in a total conversion of 94%. Other iron carbonyls, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, resulted in similar high conversions.[14] This indication that the iron carbonyls are effective catalyst precursors is supported by more recent experiments by Herrick et al. who used the iron pentacarbonyl precursor in coprocessing Illinois #6 bituminous coal with a Maya resid and found an increase in conversion to methylene chloride solubles from 39% to 82% at similar conditions to those used in the liquefaction studies but with an initial H_2 pressure of 1000 psig and a catalyst loading of 0.5 wt% Fe.

The addition of sulfur to the catalyst precursor can have a significant effect on the activity of some catalysts, particularly in the liquefaction of low sulfur coals. In the case of iron pentacarbonyl, the addition of elemental sulfur resulted in an increase of both the total conversion (~10%) and oils (~13%) for a low sulfur Wandoan coal.[13] For $W(CO)_6$, the addition of sulfur increased the conversion from 52% to 94% and the oils from 14% to 57%. At a catalyst loading of 0.4 wt% Mo the total conversion for the precursor $Mo(CO)_6$ increased by 17% while the oil yield increased by 13%. This indicates that while most of the organometallic precursors require sufficient sulfur for transformation to the active phase, the activity of iron is improved less by added sulfur than molybdenum or tungsten based precursors.

The results of some studies indicate that, even with soluble precursors, quite large crystallites or agglomerates can be formed during liquefaction and hence the potentially high dispersion is not realized or maintained. There is some evidence to indicate that, if the precursor is introduced as particulates, there is less tendency for agglomeration. Fine iron particles (50 nm mean diameter) synthesized by a flame pyrolysis technique appeared to have retained their particle size and shape during presulfiding and coal liquefaction.[16,17]

In this same context, efforts have been directed towards improving the dispersion of iron based catalyst precursors through the synthesis of ultrafine particles (UFPs) with diameters that can be significantly less than 100 nm. The increase in catalytic activity that is expected with decreasing particle size may be due to a combination of effects: an increase in exterior surface and an associated enhancement of sulfiding kinetics; a radical departure from bulk properties, especially with regard to surface energetics as the particle size is reduced below about 10 nm. The synthesis of ultrafine catalyst particles could therefore provide a means

to enhance the activity of dispersed iron (or other metal) catalysts. Several techniques have been used to produce this type of precursor, including pyrolysis in a flame or by laser.

The laser pyrolysis technique has been used to produce iron carbide UFPs from a mixture of iron pentacarbonyl and ethylene.[18] Particles of Fe_3C and Fe_7C_3 have been produced with average particle diameters of 4-20 nm. In this research, the synthesis of carbides was primarily intended as a starting point from which to establish procedures for the synthesis of oxide, sulfide, and mixed- metal phases. Although it is generally considered that the active phase of Fe and Mo is a sulfide form, recent studies by Oyama and co-workers have shown that supported and unsupported Mo carbides and nitrides exhibit high activity for hydrodenitrogenation and hydrodesulfurization reactions [19-21], raising the possibility that the carbides and nitrides of Mo and other metals may be active liquefaction catalysts.

Liquefaction studies were conducted with the Fe_3C and Fe_7C_3 UFPs using a subbituminous Wyodak coal at 385 °C, 800 psig H_2 (cold) for 15 minutes in the presence of sulfur added as dimethyldisulfide. The results of these experiments demonstrated that, under these conditions, the particles exert only a moderate catalytic effect that is slightly less than that of the oil soluble precursor iron naphthenate. At 400°C the particles increase the total conversion by ~10% above the thermal baseline. Mössbauer studies of the liquefaction residues show that, unlike the Mo carbides mentioned above, the particles are sulfided and transformed to pyrrhotite. The different response of Fe and Mo carbides to sulfiding may well relate to the much higher stability of the latter.

The moderate performance of the iron carbide UFPs may be attributable to a number of causes relating to the unusual properties of nanometer size particles, and may not be an accurate reflection of their intrinsic activity. The particles, as synthesized, are pyrophoric and the present procedure involves slow stabilization in an O_2/He mixture to allow handling in air. The method produces a surface oxide coating. Trapping the particles directly in a solvent or coal-solvent slurry may obviate this problem. The particles also tend to agglomerate, possibly aided by magnetic effects, and techniques must be developed to ensure their efficient dispersion. Thermal stability is another factor: in-situ X-ray diffraction studies have shown that sintering starts in the region of 300°C; experiments conducted under liquefaction conditions, and in the absence of coal, show that the particles are very susceptible to sintering but, in the presence of added sulfur, this tendency is reduced. Neither are there, as yet, data on the comparative kinetics of sulfiding and coal dissolution, and the prospect exists catalyst may not be present in an active form while critical reactions are taking place in the coal.

A second example of UFP synthesis is the formation of aerosol oxides formed by the combustion of metal chlorides in a hydrogen-oxygen flame.[22,23] These particles have diameters around 50 nm and surface areas between 20 and 50 m^2/g. The iron oxide aerosols have demonstrated a high catalytic activity in the presence of added sulfur at a catalyst loading of 2% for the liquefaction of a bituminous coal at 350 °C and 2000 psig H_2 (cold) for 60 minutes. The results show a doubling of the total conversion from 25% to 52%. This was only slightly less than that produced by a molybdenum aerosol generated by the same technique. This catalytic effect is reduced at higher temperatures. Again, as with the other iron based catalysts, XRD of the liquefaction residues indicate the transformation of the Fe_2O_3 aerosol to pyrrhotite in the presence of sulfur.

The use of an incipient wetness technique to impregnate the coal with Fe^{3+} from an aqueous solution has been shown to give high dispersion of the catalyst precursor on a coal substrate [24]. The coal matrix also aids in maintaining the high dispersion subsequent to activation. At a catalyst loading of 2500 ppm the precipitated FeOOH yielded the same

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catalytic activity as 1500 ppm molybdenum, added as ammonium heptamolybdate, for the liquefaction of an Illinois #6 coal at 425 °C and 2500 psig H_2 for 1 hour. The addition of sulfur was necessary to cause the transformation to the active form. The transition of amorphous iron to crystalline pyrrhotite occurred between 300° C and 350° C, although pyrrhotite is probably present below 350° C in particles with diameters less than 10 nm.

The application of Mössbauer and EXAFS spectroscopies to the study of iron based catalysts has been very informative. Studies conducted by Huffman et al. [25] used a variety of catalyst precursors including Fe_2O_3 on carbon black, $Fe_2O_3/SO_4{}^{2-}$, iron added by cation exchange, and chemical impregnation by $FeCl_3$. The primary form of the as-dispersed iron catalyst was shown to be either an oxide or oxyhydroxide. The introduction of catalyst by ion exchange techniques showed that the iron formed small crystallites of superparamagnetic FeOOH.

Modified Iron Catalysts
Another route to improving the activity of iron catalysts is to modify their composition. One approach has been to change the surface properties of hematite particles by treating a precipitated FeOOH with H_2SO_4.[26,30] Studies of these particles after calcining indicate the formation of $Fe_2O_3/SO_4{}^{2-}$. This notation denotes SO_3 chemisorbed on the surface of Fe_2O_3 in a nonstoichiometric relation. The sulfate group is believed to be responsible for the superacidity displayed by these particles. The addition of the sulfate group also leads to a decrease in the average crystallite size, which is believed to be the primary reason for their enhanced activity. Liquefaction studies using an Illinois #6 coal at 400 °C and 1000 psig H_2 (cold) for 1 hour showed an increase in the total conversion from 65 % to 90 %, in the presence of added sulfur, for a catalyst loading of 0.35 wt. %. Similar enhanced activity was seen for the liquefaction of a subbituminous Wyodak coal. Analysis of the liquefaction residues indicate that the majority of the catalyst had been transformed to pyrrhotite with only traces of oxide phases remaining.

There are a number of instances in the literature which show that metals in combination can be more effective catalysts than they are individually. The presence of titanium in the German "red mud" catalyst has been suggested to promote the activity of iron. Other research has shown that titanium can promote the activity of molybdenum, leading to significant increases in distillate production, as shown in Figure 3.[27]

It has been found that the effectiveness of an iron catalyst can be greatly improved by the addition of small concentrations of molybdenum, such that the combination has the same activity or higher than much higher concentrations of Mo alone.[28,29] The addition of 20 - 100 ppm Mo to the $Fe_2O_3/SO_4{}^{2-}$ was found to increase the oil yields as well as the total conversion in the coprocessing of an Illinois # 6 coal.[30] The incorporation of 2% Mo to the iron oxide aerosol particles formed by flame pyrolysis showed a significant increase in conversion for both a bituminous and a subbituminous coal.[31] The activity of the Mo doped aerosol particles was higher than that of a supported Ni-Mo catalysts despite the higher concentration of Mo present in the supported catalyst.

These studies have shown that by the addition of low concentrations of promoter metals, the activity of iron catalysts can be enhanced either to provide increased performance at the same concentration or equivalent performance at reduced concentrations. In either case, gains could be made at marginal extra catalyst cost which retains the "disposability" of the catalyst while effecting process economies which more than compensate.

Intermetallic hydrides have also been the subject of investigations. These alloys form reversible metal hydrides that can store molecular hydrogen within the metal matrix at

densities greater than that of liquid hydrogen. Several of these alloys have shown some activity as liquefaction catalysts.[32,33] In studies using a hvA bituminous coal, the activity of these intermetallic hydrides was shown to follow the trend $CaNi_5 = LaNi_5 > FeTi > Mg_2Cu > Mg_2Ni$, although the variation between the higher three is less than 5%. The highest activity resulted in a doubling of the total conversion over a noncatalytic baseline at temperatures between 370 °C and 427 °C. There has also been speculation that the enhanced activity of iron aerosols in the presence of added tin aerosols is due to the transitory formation of an intermetallic hydride that is unstable at room temperature.[34]

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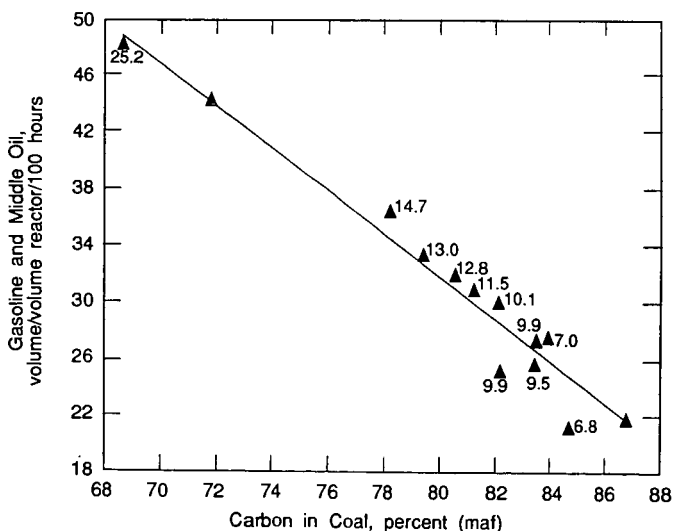
Figure 1. Yield of Gasoline Plus Middle Oil in Relation to Coal Rank
(Numbers Indicate Oxygen Content)
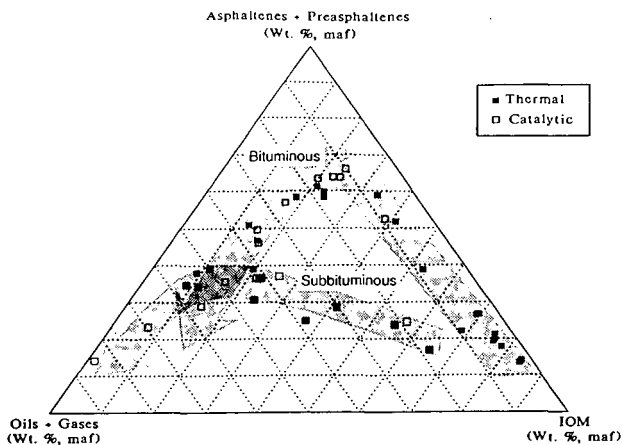
(Adapted from Wu and Storch, [2])

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Figure 2. Liquefaction Pathways for Bituminous and Subbituminous Coals.
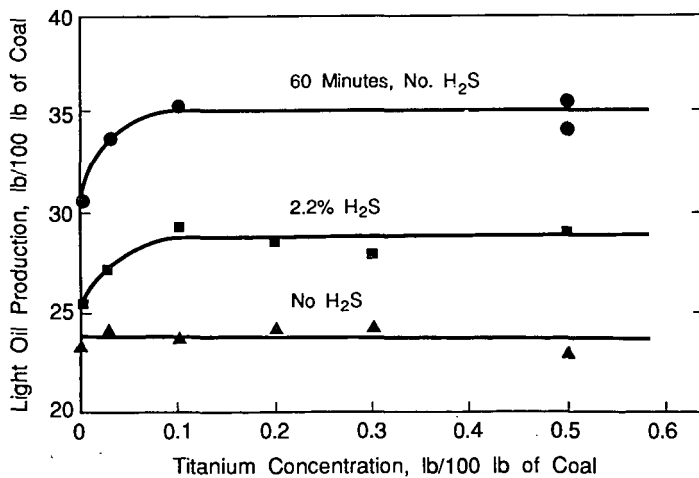*(from Keogh and Davis[7])*

Figure 3. The Promotional Effect of Titanium on Molybdenum for Light
Oil Production (0.2% Molybdenum; 480°C; 4400 psi H_2)

(From Wilson and Hurley [27])

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